

## Effective catalytic synthesis of substituted flavones and chromones using Preyssler and heteropolyacids (HPAs) as catalysts

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We report on the use of Preyssler's anion and heteropolyacids catalysts for obtaining substituted flavones and chromones for the cyclization of 1-(2-hydroxyphenyl)-3-aryl-1,3-propanediones. The reactions were performed using chloroform as solvent at reflux temperature conditions and in the absence of solvent, at 110 °C. We had excellent yields and high selectivity at these conditions. The presented synthetic method is a simple, clean and environmentally friendly alternative for synthesizing substituted flavones and chromones.

**Keywords:** Catalyst; Chromones; Flavones; Heteropolyacid; Preyssler

### INTRODUCTION

The flavonoid family has chromone structure (4*H*-benzopyran-4-one), found in nature, and the chromones are part of the flavonoid family [1]. Then flavones and chromone compounds have been reported to exhibit multiple biological properties, for example anti-HIV [2], antibacterial, antifungal, anticancer [2–4] and antitumor [5] ones. Some flavonoids inhibit the histamine release from human basophils and rat mast cells [6]. There are some methods for synthesis of the flavones and chromones, such as: the Allan-Robinson strategy, from chalcones, and via the intramolecular Wittig strategy [7, 8]. One of the most common methods involves acylation of *o*-hydroxyacetophenone with aromatic acid chloride, and it yields an aryl ester. Some reaction conditions employed were: the use of the excess sulfuric acid in glacial acetic acid, [8] cationic exchange resins in isopropanol, [9] glacial acetic acid-anhydrous sodium acetate or aqueous potassium carbonate [10]. The most interesting compounds are those that bear an aromatic ring, e.g. phenyl or substituted phenyl group in the oxygenated ring of chromone at C<sub>2</sub> (flavones) or at C<sub>3</sub> (isoflavones). The use of applicable industrial catalyst that is eco-friendly, green and simply recycled in the reaction mixtures, has been under attention in the recent decade. Thus, green chemistry has been defined as a set of principles that reduces or eliminates the use or generation of hazardous substances throughout the entire life of the chemical materials [11]. If we compare technology with

medical care, Green/Sustainable Chemistry (GSC) focuses on precaution (or prevention) rather than on diagnosis and cure [11]. Heteropolyacids (HPAs) are more active catalysts than the conventional inorganic and organic acids for various reactions in solutions [12, 13]. A variety of organic reactions, that are catalyzed by Brønsted acids, such as H<sub>2</sub>SO<sub>4</sub>, HCl, and other protonic acids, or Lewis acids such as AlCl<sub>3</sub>, FeCl<sub>3</sub>, etc., proceeded, in the presence of solid heteropolyacids or polyoxometalates, more efficiently, under milder conditions, with greater selectivity, better yields, shorter reaction times, etc. HPAs are widely applicable in the production of fine chemicals such as fragrances, pharmaceuticals, and food [13]. HPAs have been studied extensively as an efficient solid acid catalyst due to their unique advantages such as strong Brønsted acidity, structure alterability and environmental friendliness [13, 14]. Nowadays, most of the studies focus on the catalytic behaviour of the Keggin structured heteropolyacids, [15] among which the 12-tungstophosphoric acid with the H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> formula is known to be a highly active catalyst for a variety of acid-catalyzed reactions [16, 17]. In contrast, the Preyssler-structured heteropolyacid does not attract much research attention. The Preyssler's anion [NaP<sub>5</sub>W<sub>30</sub>O<sub>110</sub>]<sup>14-</sup> consists of a cyclic assembly of five PW<sub>6</sub>O<sub>22</sub> units and displays approximately D<sub>5h</sub> symmetry (Fig. 1) [18].

The advantages of Preyssler heteropolyacid as a solid acid catalyst may include large number of balanced protons, strong acidity, high hydrothermal stability, and wide pH range stability in the solution

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Ar = Phenyl, furyl, 1-Naphthyl, 2-Naphthyl  
R = H, Cl, Br, CH<sub>3</sub>, OCH<sub>3</sub>

Scheme 1. Cyclocondensation Reaction

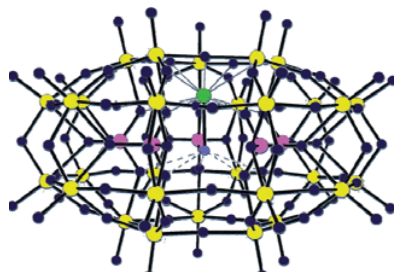


Fig. 1a

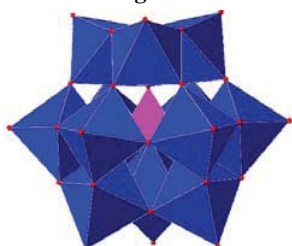


Fig. 1b

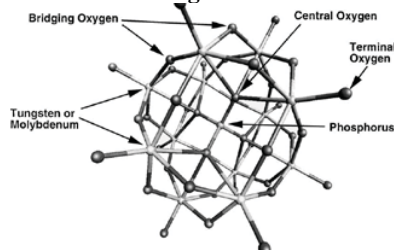


Fig. 1c

**Figure 1.** In polyhedral notation, the center of each MO<sub>6</sub> unit is a metal nucleus, and each vertex is an oxygen nucleus. The representative POM structures in polyhedral notation:

**1a)** Ball-and-stick view of [M(H<sub>2</sub>O)P<sub>5</sub>W<sub>30</sub>O<sub>110</sub>]<sup>n-</sup>, perpendicular to the C<sub>5</sub> axis, showing the position of the internal cation (green) and its associated water molecule (blue). The pink circles are the phosphorus atoms; **1b)** Keggin heteropolyanion structure [PW<sub>12</sub>O<sub>40</sub>]<sup>3-</sup>; **1c)** The Keggin unit is the primary structure of the heteropolyacid and contains 12 transition metal atoms (normally tungsten or molybdenum), a central atom (usually phosphorus), and four types of oxygen atoms: central oxygens, terminal oxygens, and two types of bridging oxygens.

[19]. A few of the researchers have investigated the catalytic performances of Preyssler heteropolyacid

in a number of organic synthesis processes [20]. Heteropolyacids have many advantages that them economical and environmentally attractive in both, academic and industrial points of view; they are useful acids and oxidation catalysts in various reactions since their catalytic features can be varied at a molecular level [21]. Among the heteropolyacids, the Keggin type [22] HPAs have been known for a long to be good catalysts for oxidation reactions [23].

## RESULTS AND DISCUSSION

Recently, we applied the heteropolyacid catalysts, the Preyssler's anion, the Preyssler mixed addenda, the Keggin and silica-supported Preyssler acid with a load from 10% to 50%, as a reusable, heterogeneous catalyst, to obtain substituted flavones and chromones for the cyclization of 1-(2-hydroxyphenyl)-3-aryl-1,3-propanediones (see Scheme 1 above).

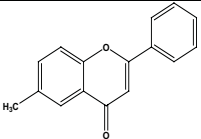
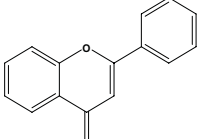
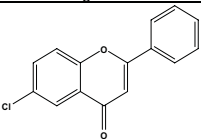
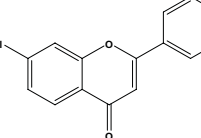
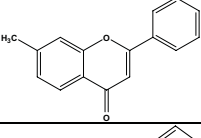
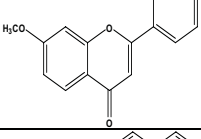
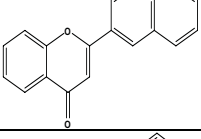
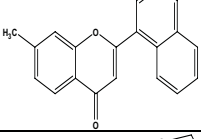
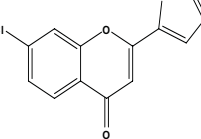
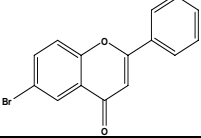
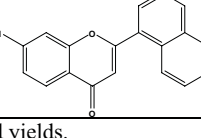
1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione was used as substrate. Different mole ratios, temperatures, and catalyst type to find the reaction optimum were tested. Cyclization reaction was not detected at room temperature. Heteropolyacid catalysts, used in diones cyclization reaction, were checked in two consecutives, and we obtained similar results and good yields in two consecutives.

Then, heteropolyacid catalysts showed almost constant activity. Also, the experiments performed in solvent-free conditions showed a substantial reduction of the reaction times. The yields of flavones were similar to those of chromones (see Tables 1 and 2 below).

This synthesis was carried out in the presence of solvent and without solvent. We obtained important results, and the yields with solvent and free solvent are very similar (Tables 1 and 2).

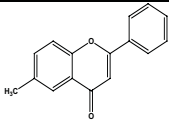
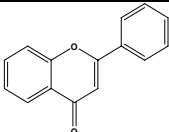
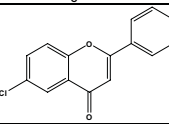
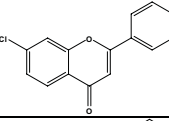
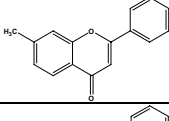
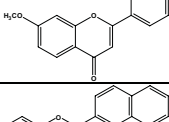
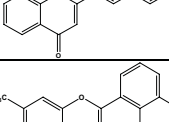
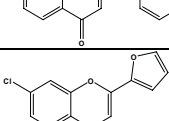
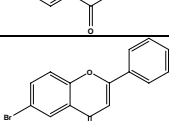
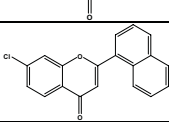
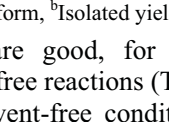
The catalyst mole ratio has not any effect on the improvement of the reaction and yields. In all the cases, the desired products were obtained at high selectivity, almost free of secondary products. We also carried out this synthesis in the presence of a solvent (Table 2). The reaction time is longer but the

**Table 1.** Preparation of flavones and chromones using heteropolyacid catalysts, Preyssler  $H_{14}[NaP_5W_{30}O_{110}]$ ,  $(H_{14}P_5)$ ,  $H_{14}[NaP_5W_{29}MoO_{110}]$ ,  $(H_{14}-P_5Mo)$ , and Keggin  $H_3[PW_{12}O_{40}]$  at reflux, solvent-free conditions

Entry	Product	<sup>a</sup> Time(min)	<sup>a</sup> Yield, %	<sup>a</sup> Yield, %	<sup>a</sup> Yield, % PW
1		30	94	92	87
2		30	96	94	88
3		30	95	92	86
4		30	94	90	86
5		30	95	90	87
6		45	91	88	84
7		45	96	92	87
8		50	97	93	89
9		50	95	90	87
10		50	91	88	86
11		50	90	80	84

<sup>a</sup>Solvent-free, <sup>a</sup>Isolated yields.

**Table 2.** Preparation of flavones and chromones using supported Preyssler catalysts  $H_{14}[NaP_5W_{30}O_{110}]$ , ( $H_{14}P_5/SiO_2$  50%,  $H_{14}P_5/SiO_2$  40%,  $H_{14}P_5/SiO_2$  30%) at reflux, solvent conditions (Solvent = chloroform, Temperature = 62 °C)

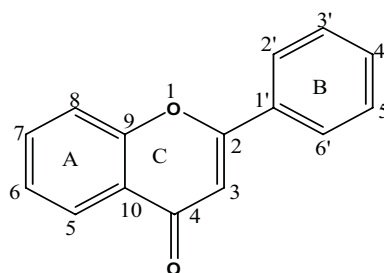
Entry	Product	<sup>b</sup> Time (min)	<sup>b</sup> Yield(%)		
			$H_{14}P_5/SiO_2$ (50%)	$H_{14}P_5/SiO_2$ (40%)	$H_{14}P_5/SiO_2$ (30%)
1		150	91	89	82
2		150	94	91	83
3		180	91	88	82
4		180	90	88	81
5		120	91	87	80
6		120	86	83	76
7		210	93	91	83
8		210	93	89	82
9		210	91	89	80
10		120	85	83	74
11		210	84	82	74

<sup>b</sup>In chloroform, <sup>b</sup>Isolated yields.

yields are good, for both, using solvent and solvent-free reactions (Tables 1 and 2).

The solvent-free conditions are more suitable in the preparation of flavones and chromones because this system is green, clean, and environmentally friendly. All compounds were characterized by melting point,  $^{13}C$  NMR and  $^1H$  NMR spectra (Table 3).

The characterisation of flavones provides an ideal application for NMR spectra with the typical skeleton, represented in Figure 2.

**Fig. 2.** Skeleton structure of the flavonoids, showing the numbering system.

**Table 3.** Spectral data for compounds of substituted flavones and chromones.

Entry	Compound	<sup>1</sup> H NMR δ (ppm) Solvent (CDCl <sub>3</sub> )	M.p(°C)
2	6-Chloroflavone	6.85 (s, 1H), 7.54-7.57 (m, 4H), 7.66 (dd, 1H, J= 2.5, 8.8 Hz), 7.91-7.93 (m, 2H), 8.20 (d, 1H, J= 2.6 Hz)	185–186 Lit.27 (183–184)
3	7-Chloroflavone	6.83 (s, 1H), 7.42 (dd, 1H, J= 1.9, 8.4 Hz), 7.52-7.56 (m, 3H), 7.62 (d, 1H, J= 1.9 Hz), 7.90-7.92 (m, 2H), 8.23 (d, 1H, J= 8.4 Hz)	159–160 Lit.28 (156–157)
4	6-Methylflavone	2.46 (s, 3H), 6.83 (s, 1H), 7.46-7.54 (m, 5H), 7.92-7.94 (m, 2H), 8.04 (s, 1H)	120–121 Lit.29;(122–123)
5	7-Methylflavone	2.45 (s, 3H), 6.76 (s, 1H), 7.20 (d, 1H, J= 9.9 Hz), 7.30 (s, 1H), 7.40-7.54 (m, 3H), 7.91-7.97 (m, 2H), 8.10 (d, 1H, J= 9.9 Hz)	122–124 Lit.30(120)
6	7-Methoxyflavone	3.93 (s, 3H), 6.97 (s, 1H), 7.05 (dd, 1H, J= 2.4, 8.8 Hz), 7.34 (d, 1H, J= 2.4 Hz), 7.58-7.61 (m, 3H), 7.94 (d, 1H, J= 8.8 Hz), 8.05-8.10 (m, 2H)	109–110 Lit.30(110)
7	6-Bromoflavone	6.83 (s, 1H), 7.52-7.54 (m, 4H), 7.84 (dd, 1H, J= 2.4, 8.3 Hz), 7.89-7.93 (m, 2H), 8.35 (d, 1H, J= 2.4 Hz)	190–191 Lit.31 (189–190)
8	2-(2-Naphthyl)chromone	6.95 (s, 1H), 7.44 (ddd, 1H, J= 1.6, 6.6, 7.9 Hz), 7.54-7.59 (m, 2H), 7.64 (d, 1H, J= 8.0 Hz), 7.74 (ddd, 1H, J= 1.6, 6.6, 7.9 Hz), 7.87-8.05 (m, 4H), 8.22 (dd, 1H, J= 1.5, 7.9 Hz), 8.46 (s, 1H)	162–163 Lit.30 (164–165)
9	7-Methyl-2-(1-naphthyl)chromone	2.50 (s, 3H), 6.65 (s, 1H), 7.26 (d, 1H, J= 9.3 Hz), 7.33 (s, 1H), 7.54-7.60 (m, 3H), 7.75 (dd, 1H, J= 0.8, 6.7 Hz), 7.92-7.95 (m, 1H), 8.03 (d, 1H, J= 8.3 Hz), 8.11-8.15 (m, 1H), 8.16 (d, 1H, J= 8.1 Hz)	162–163
10	7-Chloro-2-(1-naphthyl)chromone	6.70 (s, 1H), 7.45 (dd, 1H, J= 1.9, 8.5 Hz), 7.58-7.64 (m, 4H), 7.78 (dd, 1H, J= 1.1, 7.2 Hz), 7.97-7.99 (m, 1H), 8.05 (d, 1H, J= 8.2 Hz), 8.12-8.15 (m, 1H), 8.27 (d, 1H, J= 8.6 Hz)	198–199 Lit.30(198-199)
11	2-(2-Furyl)chromone	6.58-6.60 (m, 1H), 6.73 (s, 1H), 7.12 (d, 1H, J= 3.4 Hz), 7.39 (s, 1H), 7.46 (d, 1H, J= 8.3 Hz), 7.61-7.67 (m, 2H), 8.21 (dd, 1H, J= 1.2, 7.5 Hz)	134–135 Lit.32(135)

Flavones are a class of natural substances which occur frequently in plants and which have 15 C atoms in their framework. The nine double-bond equivalents which are contained in the empirical formula, <sup>1</sup>H, signals in the region appropriate for shielded benzene ring protons (5.9-6.9 ppm). The <sup>1</sup>HNMR spectra of flavones showed a singlet at 6.55-6.8 due to 1H of 3H, i.e. pyrone ring; it is the characteristic singlet for flavones. The multiple at 7.1-7.9 is due to aromatic protons. The patterns of the aromatic protons reveal the nature of substitution of the various aromatic systems. The chemical shifts of the protons of rings A and B are independent one from another but are affected by ring C. Peaks arising from A occur upfield, and are easily recognised, therefore examination of an unfamiliar spectrum usually starts with recognition of these peaks. Remaining peaks in the aromatic region reveal the pattern of oxygenation of ring B and confirm the nature of ring C. The C-6 and C-8 resonances in flavones appear at between 92 and 100 ppm with C-6 downfield relative to C-8 resonance. The <sup>1</sup>H NMR spectrum shows that the presence of the double bond in ring C of flavones causes a marked downfield shift of the 6,8 protons, producing a two-doublet pattern. In flavones, the presence of the C-ring double bond causes shift of the 2',6'-protons and the spectrum shows the two complex multiplets, one centered at <sup>1</sup>H 8.0 (2',6') and the other at <sup>1</sup>H 7.6 (3',4',5'). In the reactions,

spectroscopic data (<sup>13</sup>C NMR) for authentic samples are as follows:

**Flavone:** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):

δ = 107.3 (C - 3), 117.9 (C - 8), 123.7 (C - 10), 124.9 and 125.5 (C - 6 or C - 5), 126.0 (C - 2' and C - 6'), 129.0 (C - 3' and C - 5'), 131.8 (C - 1' and C - 4'), 133.5 (C - 7), 155.9 (C - 9), 163.1 (C - 2), 177.9 (C=O).

**7-methoxyflavone :** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ= 56.3 (CH<sub>3</sub>-O), 101.1 (C - 8), 106.9 (C - 3), 114.9 (C - 6), 117.3 (C - 10), 126.3 and 126.4 ((C - 2' and C - 6') or C - 5), 129.3 (C - 3' and C - 5'), 131.3 and 131.8 (C - 1' or C - 4'), 157.7 (C - 9), 162.3 (C - 2), 164.1 (C - 7), 176.6 (C=O).

**6-Chloroflavone :** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 107.5 (C - 3), 119.9 (C - 8), 125.0 (C - 5), 125.2 (C - 10), 126.3 (C - 2' and C - 6'), 129.1 (C - 3' and C - 5'), 131.2 and 131.4 (C - 6 or C - 1'), 131.9 (C - 4'), 134.0 (C - 7), 154.5 (C - 9), 163.6 (C - 2), 177.2 (C=O).

**6-methylflavone :** <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ= 22.0 (CH<sub>3</sub>), 107.5 (C - 3), 118.0 (C - 8), 122.0 (C - 10), 126.0 (C - 5), 127.2 (C - 2' and C - 6'), 129.0 (C - 3' and C - 5'), 131.7 and 132.0 (C - 4' or C - 1'), 135.2 (C - 6), 145.1 (C - 7), 156.3 (C - 9), 163.2 (C - 2), 178.2 (C=O).

#### CATALYST REUSABILITY

The catalyst could be recovered by a simple filtration at the end of the reaction. The recycled

catalyst could be washed with dichloromethane and used in a second run of the reaction process.

#### Catalyst preparations

All the chemicals were purchased from Merck Company. All the chemical compounds and Keggin type heteropolyacids were acquired from commercial sources. Preyssler,  $H_{14}[NaP_5W_{30}O_{110}]$ , ( $H_{14}-P_5$ ),  $H_{14}[NaP_5W_{29}MoO_{110}]$ , ( $H_{14}-P_5Mo$ ) and supported Preyssler on silica,  $H_{14}P_5/SiO_2$  were prepared in accordance with the earlier reports [24-27].

## EXPERIMENTAL

#### Instruments

The  $^1H$ -NMR spectra were recorded on an FT-NMR Bruker 250 MHz Aspect 3000 spectrometer, and  $^1H$  NMR and  $^{13}C$  NMR spectra were recorded at 298°K. The melting points were recorded on an Electrothermal type 9100 melting point apparatus, and were uncorrected. Chemical shifts were reported in ppm ( $\delta$ -scale) relative to the internal standard TMS (0.00 ppm); the solvent was used as a reference. TLC was carried out with E. Merck Silica gel GOF-254 (0.25 mm thickness) pre-coated tic plates. The column chromatography was carried out with the silica gel (Kieselgel 60, 70-230 mesh, E. Merck).

The progress of the reaction was monitored by TLC and all the products were identified by comparison of their physical and spectroscopic data with those reported for authentic samples. All the yields were calculated from crystallized products.

## GENERAL PROCEDURES

#### Preparation of substituted flavones and chromones without solvent

1,3-diketone (0.7 mmol) was dissolved in catalyst (0.3 mmol), then the mixture was stirred at reflux temperature (110 °C) for different time periods (Table 1), and this mixture was extracted (via) warm toluene (3 × 5 mL). The extracted compounds were washed, first with 3M NaOH, then with  $H_2O$ , and dried over  $MgSO_4$ . The pure products were obtained by column chromatography. The residue was isolated by the chromatograph on the silica column and thus favones and chromones were obtained. The residue was chromatographed on the silica column ( $CH_2Cl_2:CHCl_3=70:30$ ) and two components were obtained. All the solid crude products were recrystallized from methanol.

#### Preparation of substituted flavones and chromones in solvent

1,3-diketone (0.7 mmol) was dissolved in chloroform (5 mL), then the catalyst (0.3 mmol) was added to the solution. The reaction mixture was heated and stirred at reflux temperature (60–62°C) for different time periods (Table 2). After completion of the reaction, the catalyst was filtered off, washed with ethyl ether (3×10 mL), and the solvent was subjected to evaporation. The extracts were combined and washed with 3M NaOH, then with  $H_2O$ , and dried over  $MgSO_4$ . The organic solution was concentrated in the vacuum. The pure products were obtained by column chromatography. The residue was isolated by the chromatograph on the silica column and thus favones and chromones were obtained. The residue was chromatographed on the silica column ( $CH_2Cl_2:CHCl_3 =70:30$ ) and two components were obtained. All the solid crude products were recrystallized from ethanol. All products were identified with those, reported for authentic samples, by comparison of their physical and spectroscopic data.

## CONCLUSION

The Preyssler silica supported catalyst and Keggin heteropolyacid catalysts provide very good and appropriate yields in this reaction. These catalysts are reusable, recyclable, and they separate and recover easily for further use; they are green, environmentally friendly, inexpensive, non-corrosive, solid - with higher acidic strength than the mineral acid; they are of high thermal stability; they produce low waste and oxidation, and reduced effectiveness. The catalyst properties are constant. The catalysts, based on the supported tungstophosphoric and molybdo-phosphoric acids, showed catalytic activity for the reaction of cyclization of 1-(2-hydroxyphenyl)-3-aryl-1,3-propanediones. The conversion to flavones and substituted chromones was in general higher in homogeneous phase than that observed for the supported catalysts.

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## ЕФЕКТИВНА СИНТЕЗА НА СУБСТИТУИРАНИ ФЛАВОНИ И ХРОМОНИ ЧРЕЗ ПРАЙСЛЕРОВИ АНИОНИ И ХЕТЕРО-ПОЛИКИСЕЛИНИ КАТО КАТАЛИЗАТОРИ

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(Резюме)

Съобщава се за използването на Прайслерови аниони и хетеро-поликиселини като катализатори на получаването на флавонови и хромони чрез циклизирането на 1-(2-хидроксифенил)-3-арил-1,3-пропандиони. Реакциите се извършват, като се използва хлороформ като разтворител с рециркуляция или в отсъствие на разтворител при 110°C. Постигнати са отлични добиви и висока селективност. Настоящият метод е проста, чиста и съобразена с околната среда алтернатива за синтезата на субституирани флавонови и хромони.